Polymer Science

ADSORPTION OF SHORT TWO-DIMENSIONAL COMPACT CHAINS*

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Abstract Short two-dimensional compact chains adsorbed on the attractive surface at different temperatures were investigated by using the enumeration calculation method. First we investigate the chain size and shape of adsorbed chains, such as characteristic ratios of mean-square radii of gyration $\langle S^2\rangle_x/N$ and $\langle S^2\rangle_y/N$, shape factor $\langle\delta\rangle$, and the orientation of chain bonds $\langle\cos^2\theta\rangle$ to illuminate how the size and shape of adsorbed compact chains change with increasing temperatures. There are some special behaviors for the chain size and shape at low temperature, especially for strong attraction interaction. In the meantime, adsorbed compact chains have different behaviors from general adsorbed polymer chains. Some thermodynamics properties are also discussed here. Heat capacity changes non-monotonously, first increases and then reduces. The transition temperature T_c is nearly 1.0, 1.4, 2.0 and 4.2 (in the unit of T_0) for the case of $\varepsilon = 0$, -1, -2 and -4 (in the unit of kT_0), respectively. Average energy per bond increases while average Helmholtz free energy per bond decreases with increasing temperatures. From these two thermodynamics parameters we can also get another transition temperature T_c', and it is close to 0.7, 1.1, 1.5 and 3.4 for $\varepsilon = 0$, -1, -2, and -4, respectively. Therefore, T_c is greater than T_c' under the same condition. These investigations may provide some insights into the thermodynamics behaviors of adsorbed protein-like chains.

Keywords: Adsorption of compact chain; Enumeration calculation method.

INTRODUCTION

The adsorption phenomenon has been a subject of intensive study because of its importance in many areas of science including physics, chemistry, biology, material science and tribology. This phenomenon is widely applicable for stabilizers or flocculationg agents for colloidal dispersions[1], polymer adhesion[2], biocompatibility[3] and chromatographic separation. Furthermore, adsorption has distinct phase transition properties and thus provides a realistic system for the fundamental understanding of the statistical mechanics of phase transitions. At the same time, protein adsorption bears some resemblance to the adsorption of polymers, and particularly that of copolymer and polyelectrolytes. Protein adsorption is a widespread and interesting process which is not completely understood yet[4]. In fact protein adsorption plays a key role in a variety of biological processes[5], and is of primary importance in many practical applications such as the deposition of blood proteins on to medical devices, the subsequent modification of their biological responses, the bacterial fouling of ships hulls, the blockage of filtration membranes in bioseparation processes, the design of biocompatible materials[6], drug carriers[7] and biosensors[8], among many others. Furthermore, preferential adsorption plays a key role in separation techniques such as chromatography[9].

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In recent years, numerous experimental and theoretical works have been devoted to the study of protein adsorption phenomenon onto solid surfaces. The scientists could experimentally measure these parameters more and more accurately as many excellent experimental techniques have been developed to study the adsorption phenomenon. The relevant experimental apparatus such as atomic force microscopy (AFM) [10] has been used widely to study the adsorption phenomenon. In the meantime, with the advancement of computer technology, more and more computer simulations are widely adopted to study statistical properties of polymer chains. In this paper, the adsorption behavior of short two-dimensional compact chains will be discussed in terms of enumeration calculation method, which can help us to understand the adsorption phenomenon in detail. Here the compact polymers are adopted because they are the main structure of globular proteins[11]. Since large polymer chains have countless conformations, this calculation method can only calculate short chains, and our purpose is to use the behavior of short chains to predict that of long chains.

CALCULATION METHOD

According to the model of a self-avoiding chain of length N on square lattice, the Hamiltonian of the compact chains system with adsorption interaction can be defined as:

$$E = \sum_{i<j} \varepsilon_{ij} \Delta(r_i - r_j) + V \tag{1}$$

where ε_{ij} is the contact energy between monomer i and j, and $\Delta(r_i - r_j) = 1$ if r_i and r_j are adjoining lattice sites with i and j not adjacent along the chain, while $\Delta(r_i - r_j) = 0$ otherwise[11]. In general, $\varepsilon_{ij} = -1$ (in the unit of kT_0). In order to simulate the adsorption of compact chains, it is realized by introducing attractive contact potential between the surface and chain segments. The additional item V in Eq. (1) represents the adsorption interaction. In this paper, we adopt the short two-dimensional compact chains model so the potential applied in lattice models also can be rewritten as:

$$V(y_i) = \begin{cases} 0, & y_i > 1 \\ \varepsilon, & y_i = 1 \end{cases} \tag{2}$$

where y_i is the distance between i-th monomer in a chain and the adsorption surface and ε is the value of adsorption energy accordingly. In our calculation, we employ the adsorption energy $\varepsilon = 0$, -1, -2, and -4 (in the unit of kT_0), respectively. Here we only discuss short two-dimensional compact chains, so the x-axis certainly means the adsorption surface and the y-axis is vertical to this surface. Because of the enumeration calculation method we could count all conformations of the short two-dimensional compact chains with different chain length and different adsorption energy.

The partition function of the system is

$$Z = \sum_i exp(-E_i / kT) \tag{3}$$

where $\sum_i$ is the sum of all conformations. In fact, the partition function was widely used to study the thermodynamic properties, and this parameter is closely related to the number of conformations. In this paper we only calculate the short compact chains with chain length N = 13, 16 and 19, respectively. From the partition function, we can derive the Helmholtz free energies of adsorbed compact chains:

$$A = -kT \ln Z \tag{4}$$

This parameter can provide much important thermodynamic information for adsorbed compact chains[12–14].

RESULTS AND DISCUSSION

Chain Size and Shape

We first calculate the parallel and perpendicular mean square radii of gyration of the adsorbed chains, which are defined as

$$< S^2 >_x = < \frac{1}{N+1} \sum_{i=0}^{N} (x_i - x_{\text{c.m.}})^2 > \tag{5}$$

$$< S^2 >_y = < \frac{1}{N+1} \sum_{i=0}^{N} (y_i - y_{\text{c.m.}})^2 > \tag{6}$$

where (x_i, y_i) are the coordinate of the i-th monomer in a chain and $(x_{\text{c.m.}}, y_{\text{c.m.}})$ are the position of the center of mass of the chain. The angular brackets < > denote thermodynamic average. Figure 1 shows the mean-square radii of gyration $<S^2>_x/N$ and $<S^2>_y/N$ as a function of temperature T with different adsorption energies and different chain lengths. Firstly, we discuss $<S^2>_x/N$ in Fig. 1(a). The curves with $\varepsilon = -1$, -2, and -4 all decrease with increasing temperatures T, especially at low temperature. However, the curves with $\varepsilon = 0$ increase with increasing temperature T at low temperature. Contrary results are obtained for $<S^2>_y/N$ in Fig. 1(b). All the curves in Fig. 1(b) increase with increasing temperatures T and they increase abruptly at low temperature and slowly at high temperature. For a given adsorption energy all the curves almost get together at low temperature and start to separate with different chain lengths at high temperature. When $\varepsilon = 0$, the behavior of $<S^2>_y/N$ is similar to $<S^2>_x/N$. The parallel and perpendicular mean square radii of gyrations both increase at low temperature. The reason may be that the general compact chains will expend toward two directions of two-dimensional space with increasing temperatures. For the other cases of $\varepsilon = -1$, -2 and -4, the ratio of $<S^2>_y/N$ also increase abruptly with increasing temperatures at low temperature, which is contrary to $<S^2>_x/N$ at the same region. This means that at low temperature most of the monomers are adsorbed by x-axis, even when adsorption energy becomes $\varepsilon = -2$, and -4, $<S^2>_y/N$ are approaching zero at $T = 0.6$, which illustrates that all monomers in chains almost lie on the adsorption surface. When temperature increases, the chains tend to move in the direction of y-axis and this leads $<S^2>_x/N$ to reduce and $<S^2>_y/N$ to increase. At last the parallel and perpendicular mean square radii of gyration of adsorbed chains become equal, *i.e.*, $<S^2>_x/N \approx <S^2>_y/N$ at high temperature.

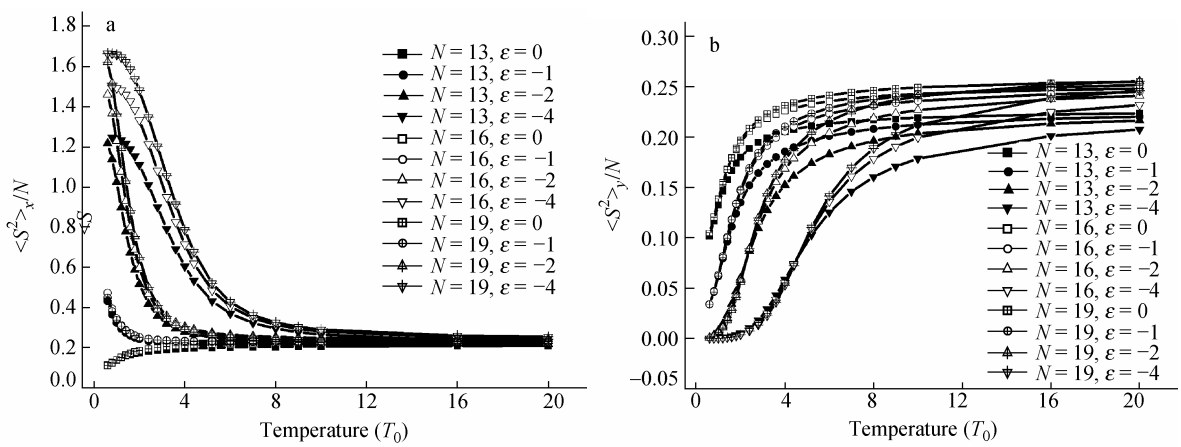

Fig. 1 Mean-square radii of gyration per bond $<S^2>_x/N$ (a) and $<S^2>_y/N$ (b) as a function of temperature T for adsorbed compact chains with different chain lengths N and adsorption energies ε

In order to investigate the shape of adsorbed chains in more detail, here we consider the radius of gyration tensor S, which is defined as:

$$S = \frac{1}{N+1}\sum_{i=0}^{N} S_i S_i^T = \begin{pmatrix} S_{xx} & S_{xy} \\ S_{yx} & S_{yy} \end{pmatrix} \tag{7}$$

Here $S_i = col(x_i, y_i)$ is the position of monomer i in a frame of reference with its origin at the center of mass. The tensor S can be bisected to form a diagonal matrix with two eigenvalues L_1^2 and L_2^2 ($L_1^2 \le L_2^2$). Solc and Stockmayer first used these parameters in three-dimension $<L_1^2>:<L_2^2>:<L_3^2>$ to measure the shape of flexible polymer chains, and they estimated the ratio to be 1:2.7:11.7 based on a random walk of 100 bonds on a simple cubic lattice using Monte Carlo (MC) technique. Using these parameters the characteristic of the chain shape may be obtained by combining the reduced components to a single quantity that varies between 0 (sphere) and 1 (rod). In our two-dimensional model we rewrite $<\delta>$ as [15]:

$$<\delta> = 1 - 4 < \frac{L_1^2 L_2^2}{(L_1^2 + L_2^2)^2} > \tag{8}$$

Figure 2 presents the value of $<\delta>$ as a function of temperature T for adsorbed chains with different chain lengths and different adsorption energies. For the case of $\varepsilon = 0$, the value of $<\delta>$ is about 0.2 at low temperature. In fact, if the compact chains are free to move and are not restricted in two-dimensional space with $y > 0$, the value of $<\delta>$ is approaching zero. However, in our calculation the chains are not allowed to penetrate through the y-axis, so our adsorbed chains will have a different result of $<\delta> \approx 0.2$. With increasing temperatures, $<\delta>$ also increases until this value reaches to about 0.5 at high temperature. When the adsorption interaction affects compact chains, the results show different behaviors in Fig. 2. At low temperature, $<\delta>$ reduces from 0.7 to 0.5 for $\varepsilon = 0$ or 1, and from 1.0 to 0.5 for $\varepsilon = -2$ or -4. When adsorption energy is strengthened at a given temperature $<\delta>$ increases. For a strong adsorption energy, the whole compact chain is pulled down on x-axis, so its shape changes from sphere in the two-dimensional space (without adsorption) to rod lying on x-axis (with strong adsorption) completely at once. The shape can be changed from rod to sphere again with increasing temperatures because as temperature increases the chains would like to move but not to be adsorbed on the surface. Moreover, this change is more obvious with stronger adsorption energy and is independent of chain length N.

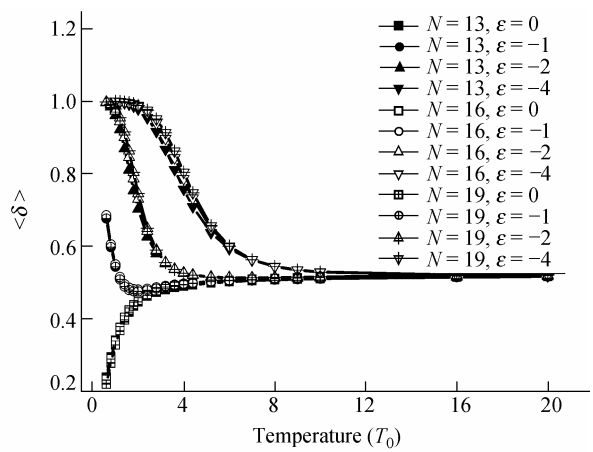

Fig. 2 $<\delta>$ as a function of temperature T for adsorbed compact chains with different chain lengths N and adsorption energies ε

In order to investigate the orientation of chain bond, another parameter: $<\cos^2\theta(y)>$ is calculated; here θ is the angle between the bond and the y-axis, and the results are shown in Fig. 3. From the above definition, we know that if $<\cos^2\theta(y)> = 0$, this means $\theta = 90°$ for all bonds, and they all are parallel to x-axis (the adsorption surface). The curves in Fig. 3 show $<\cos^2\theta(y)>$ as a function of temperature T for adsorbed chains with different y layers and different adsorption energies. Generally, $<\cos^2\theta(y)>$ increases with increasing temperatures

and decreases with distance y from the surface at a given temperature. For a strong adsorption energy, the curves start from zero, implying that the direction of chain bond is parallel to x-axis at low temperature.

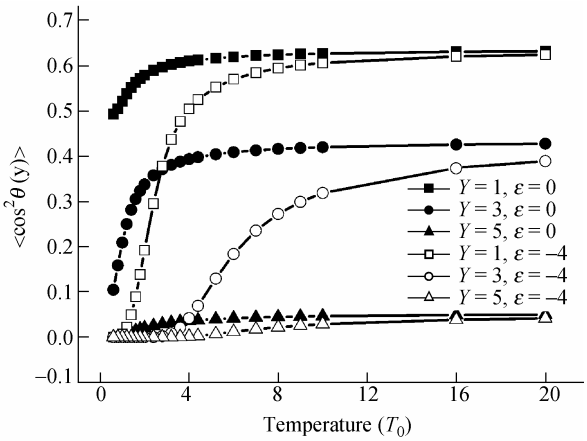

Fig. 3 $<\cos^2\theta(y)>$ as a function of temperature T for adsorbed compact chains with different chain lengths N and adsorption energies ε

In the above discussion, we have used some available parameters to analyze the change of the chain shape and size with different adsorption energies. In general, we can get three conclusions: firstly, the behavior of compact chain without adsorption energy is far different from the adsorbed chain. Secondly, the adsorption energy affects the shape and size obviously especially for strong attractive interaction. Lastly, in spite of different chain lengths and adsorption energies, the chains will all tend toward the stable state so the size and shape will also fix in one stable value at high temperature.

Thermodynamics Properties

First, we discuss the heat capacity C_v, which is defined as[16]:

$$C_v = \frac{< E^2 > - < E >^2}{kT^2} \tag{9}$$

C_v plays a central role in chain stability calculations, and is the most neglected quantities of all the thermodynamic properties in experimental and theoretic investigation. Furthermore, heat capacity contains valuable information about the monomer arrangement. Our results are shown in Fig. 4. Though the numerical values of C_v in Fig. 4 are different, all the curves change non-monotonically that C_v first increases at low temperature and then reduces to minimum at high temperature. The coil-to-globule transition temperature T_c can be estimated from the location of the main peak on the heat capacity plot as a function of temperature[13, 16]. During temperature increase, the curves disclose the phase transformation of short compact chain visually. In terms of different adsorption energies, 12 curves can be divided into four classes according to the shapes. The transition temperature T_c is nearly 1.0, 1.4, 2.0 and 4.2 (in the unit of T_0) in the case of ε = 0, –1, –2 and –4, respectively. The crests move to the right with increasing temperatures, but the transition temperatures T_c are fixed with increasing chain lengths. The phase transformations change more greatly with stronger adsorption energy. When $\varepsilon = 0$, the difference of the heat capacity for $N = 19$ between maximum and minimum is 2.0, while this difference increases to 22.8 for $\varepsilon = -4$. The adsorption energy affects the phase transformation greatly. Besides the main peak corresponding to the collapse transition, there is also a secondary peak at a lower temperature. This secondary peak presumably describes the roughening transition[17]. In our paper, we adopt enumeration calculation method, which can only calculate short compact chains. This leads to the disappearance of the secondary peak. The results of these microscopic calculations may explain some macroscopic phenomena of adsorption of compact chains, and can provide some insights into the adsorption of proteins.

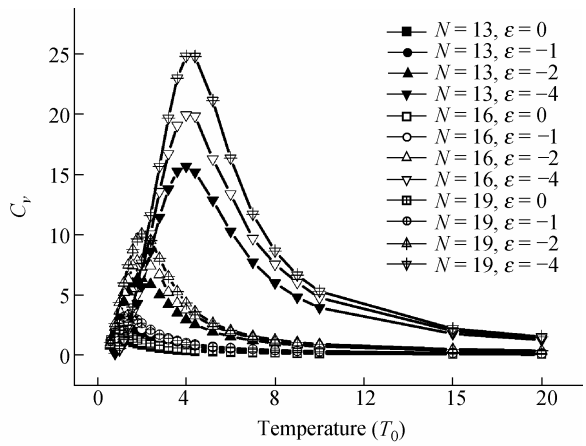

Fig. 4 Heat capacity C_v as a function of temperature T for adsorbed compact chains with different chain lengths N and adsorption energies ε

In Fig. 5 the average energy per bond for adsorbed chains with different chain lengths and different adsorption energies is calculated. In our paper, energies for adsorbed compact chains include contact energy and adsorption energy. Average energies per bond increase with increasing temperatures specially at low temperature, and then tend toward a constant value. At a given temperature, the average energy per bond also increases with increase in adsorption energy. According to the discussion about chain shape and size, the absorbed compact chain will leave x-axis (the adsorption surface) with increasing temperatures, which leads to the decrease in the number of adsorbed monomers accordingly. This movement could approach the stable state at certain temperature region. From this figure, we can also get the same conclusion in terms of the viewpoint of average energy. On the other hand, the largest slope obtained from the tangents of the curves in Fig. 5 is selected to calculate the corresponding temperature value. We define this temperature as T_c' to distinguish it from the transition temperature T_c in Fig. 4. T_c and T_c' may have some relevance to the glass-liquid transition temperature T_g[18–20]. T_c's of 0.7, 1.1, 1.5 and 3.4 for different adsorption energies ε = 0, −1, −2 and −4, respectively, are obtained. In Fig. 5 we also give an example for ε = −4, and N = 19. T_c' = 3.4 is indicated by a dash line in Fig. 5. Compared with the results in Fig. 4, T_c' is smaller than the corresponding transition temperature T_c. Moreover, it seems that the average energy per bond is not related to chain length, and only at high temperature the curves differ from one another slightly. This result agrees well with the above discussion.

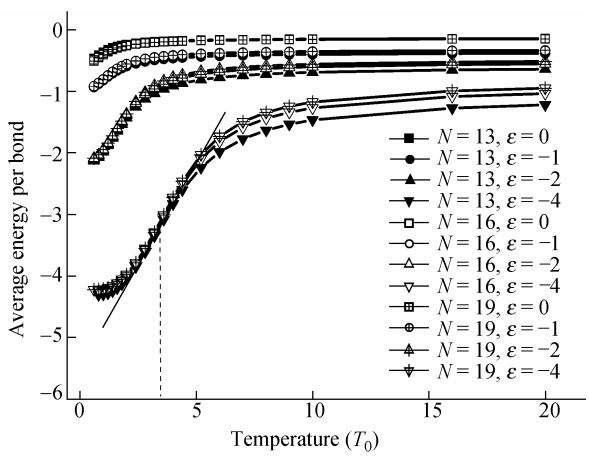

Fig. 5 Average energy per bond as a function of temperature T for adsorbed compact chains with different chain lengths N and adsorption energies ε

Finally, we investigate the average Helmholtz free energy per bond for adsorbed chains with different chain lengths and different adsorption energies. The change of conformations leads to the change of thermodynamics properties of adsorbed chains. According to Eq. (4), we plot average Helmholtz free energy per bond as a function of temperature T for adsorbed chains with different chain lengths and different adsorption energies in Fig. 6. In spite of the very small difference between the curves, especially at high temperature, we can classify the curves into four classes in terms of different adsorption energies. When temperature is low, the curves have a small curvature, the camber changes more obvious with increase in adsorption energy. Even at a low temperature region, A/N can be regarded as a constant, and the curves become straight lines at high temperature. The slopes for these lines only range from –0.826 to –0.878. From Eq. (4), we can get the following equation at high temperature:

$$A/N = (-T\ln Z)/N = -\alpha T \tag{10}$$

here α presents the absolute value of the slope of the fit line (k = 1 in Eq. (4)). According to Eq. (10), we can conclude that the relation between the partition function and the chain length at high temperature is as follows:

$$Z \propto \mathrm{e}^{\alpha N} \tag{11}$$

This is a meaningful result. As we all know that though the enumeration calculation method can uncover the characteristic of compact chains more completely and accurately than others such as the MC method, which is impossible to calculate the long chains by using the enumeration calculation method because the computer technique could not follow up with the increase in conformations. According to the above equation, we can

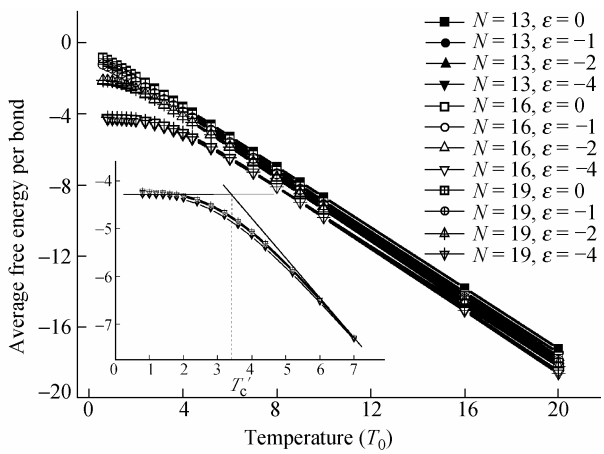

Fig. 6 Average free energy per bond as a function of temperature T for adsorbed compact chains with different chain lengths N and adsorption energies ε

obtain the partition function of long compact chains. Our investigation pertaining to short compact chains can be used as a guide for studying long chains. We can also obtain the temperature of 0.7, 1.1, 1.5 and 3.4 for adsorbed chains with different adsorption energies ε = 0, –1, –2 and –4, respectively, and the results agree well with the conclusion in Fig. 4. We also add the illustration of ε = –4 and N = 19 in Fig. 6; the dash line also points to the same temperature value about T_c' = 3.4. The analogous method is widely used to calculate the vitrification point.

This investigation can provide some insights into the adsorption behavior of compact chains.

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